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Quinone Imides. XVIII. *p*-Quinonedipivalimides and their Reactions

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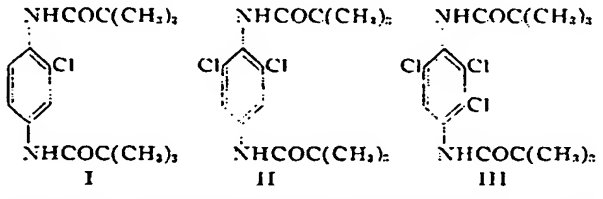
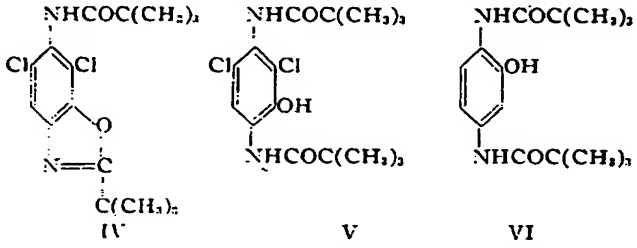
2-Chloro-*p*-quinonedipivalimide reacts with hydrogen chloride to give exclusively 2,6-dichloro-*p*-phenylenedipivalamide. Oxidation of this latter product to the corresponding diimide followed by addition of hydrogen chloride yields a mixture which was separated chromatographically into 2,6-dichloro-*p*-phenylenedipivalamide, 2,3,5-trichloro-*p*-phenylenedipivalamide and 2-*t*-butyl-5,7-dichloro-6-pivalamidobenzoxazole. The oxazole with alkali gives 3,6-dipivalamido-2,4-dichlorophenol, the constitution of which was proved by non-identity with the other two dichloroisomers and synthesis by chlorination of 2,5-dipivalamidophenol. 2,3-Dichloro- and 2,5-dichloro-*p*-quinonedipivalimides prepared from the corresponding diamines by introduction of pivalyl groups, then oxidation, add hydrogen chloride readily to give an excellent yield of the 2,3,5-trichloro diamide. They, as well as the unchlorinated diimide, add formic acid to yield formoxy diamides which hydrolyze to the corresponding phenols. The 2,3,5-trichloro-*p*-quinonedipivalimide adds hydrogen chloride to give a mixture of 2,3,5,6-tetrachloro-*p*-phenylenedipivalamide and 2-*t*-butyl-4,5,7-trichloro-6-pivalamidobenzoxazole.

In previous papers various *p*-phenylenedibenzimides[2] and their adducts with hydrogen chloride were described. Characteristic of the 2-chloro-*p*-quinonedibenzimide[2b] when it reacts with hydrogen chloride is the exclusive formation of the 2,6-dichloro-*p*-phenylenedibenzamide. In contrast, the corresponding dibenzenesulfonyl, dicarbethoxy and dicarbobenzoxy derivatives of 2-chloro-*p*-quinonediimine yield isomeric mixtures of dichloro compounds. With the dibenzenesulfonyl diimide the 2,5-dichloro diamide predominates. Unlike the other analogs also is the fact that 2,6-dichloro-*p*-quinonedibenzimide reacts with hydrogen chloride to give a complicated mixture of products from which only a small amount of trichloro-*p*-phenylenedibenzamide was isolated.

A similar study has now been made with *p*-phenylenedipivalamide. This substance was oxidized in the usual way with lead tetraacetate in chloroform to the diimide which added hydrogen chloride to give the 2-chloro-*p*-phenylenedipivalamide (I). Oxidation of I took place readily to the corresponding diimide which added hydrogen chloride to give exclusively 2,6-dichloro-*p*-phenylenedipivalamide (II). The structure of II was established by synthesis from 2,6-dichloro-*p*-phenylenediamine by the introduction of two pivalyl groups. The diimide from II, like the corresponding dibenzoyl derivative, reacted with hydrogen chloride to give a complicated mixture. This mixture was separated by repeated crystallizations into (1) a mixture of 2,6-dichloro-*p*-phenylenedipivalamide (II) and 2,3,5-trichloro-*p*-phenylenedipivalamide (III), (2) 2-*t*-butyl-5,7-dichloro-6-pivalamidobenzoxazole (IV) and (3) 3,6-dipivalamido-2,4-dichlorophenol (V). Chromatographic separation was more satisfactory. If the excess of hydrogen chloride was removed from the initial reaction mixture and petroleum ether and ether added to high dilution, the products could be adsorbed on an alumina column. Elution resulted in isolating first the 2-*t*-butyl-5,7-dichloro-6-pivalamidobenzoxazole (IV), then the 2,3,5-trichloro-*p*-phenylenedipivalamide (III) and finally the 2,6-dichloro-*p*-phenylenedipivalamide (II). No 3,6-dipivalamido-2,4-dichlorophenol (V) was obtained. Either the phenol was formed by hydrolysis of the oxazole during the fractional crystallization or it was not eluted from the column under the solvent conditions used. The phenol (V) was readily acetylated; it was dehydrated to the oxazole (IV) merely by heating with ethylene glycol. The oxazole (IV) was hydrolyzed by alkali to the phenol (V).



I II III



IV V VI

p-Quinonedipivalimide, like the dibenzoyl analog,[3] reacted with acetic acid when permitted to stand at room temperature in that solvent. The resulting product was 2-acetoxy-*p*-phenylenedipivalamide. Upon hydrolysis, the acetyl group was removed and 2,5-dipivalamidophenol (VI) was formed. Formic acid, in a similar manner, gave the formoxy derivative which hydrolyzed to the same phenol. The phenol (VI) was stable to heating in ethylene glycol but upon being held above its melting point it was converted with the loss of water to the corresponding oxazole (VII); the oxazole with aqueous alkali reverted to the phenol.

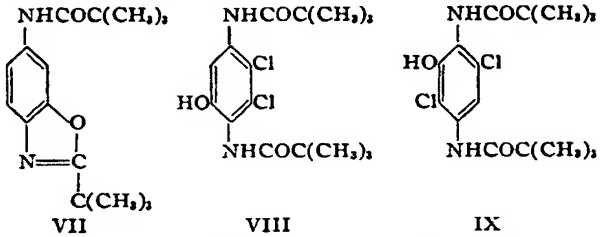
The structure of the phenol (V) was established by indirect evidence and by synthesis. 2,3-Dichloro-*p*-phenylenedipivalamide and 2,5-dichloro-*p*-phenylenedipivalamide were both synthesized by introduction of pivalyl groups into the corresponding diamines. These were readily oxidized to the corresponding diimides. To these latter, in contrast to the 2,6-isomer, hydrogen chloride was added to give excellent yields of the 2,3,5-trichloro-*p*-phenylenedipivalamide. The 2,3- and 2,5-di-

(1) An abstract of a thesis submitted by John Morrow Stewart to the Graduate College of the University of Illinois, 1952, in partial fulfillment of the requirements for the Degree of Doctor of Philosophy; Eastman Kodak Fellow, 1951-52.

(2) (a) R. Adams and J. L. Anderson, THIS JOURNAL, **72**, 5154 (1950); (b) R. Adams and D. S. Acker, *ibid.*, **74**, 3029 (1952).

(3) R. Adams and D. S. Acker, *ibid.*, **74**, 3657 (1952).

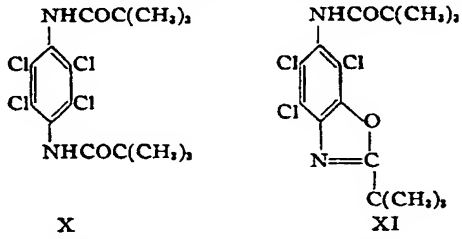
chloro diimides reacted with formic acid in the same manner as the unchlorinated diimide and upon hydrolysis of the products the two phenols, VIII and IX, resulted. Neither of these was identical with that formed by the reaction of hydrogen chloride with the 2,6-dichlorodiimide. The only other isomer is that proposed in formula V. Attempts failed to add acetic acid or formic acid to 2,6-dichloro-*p*-quinonedipivalimide in the same way in which the 2,3- and the 2,5-isomers reacted. If, however, 2,5-dipivalamidophenol (VI) was chlorinated, it was not difficult to separate from the resulting mixture by its preferential solubility in sodium bicarbonate, the third dichloro isomer which was identical with V.



VII VIII IX

It is probable that the complicated mixture obtained by treatment of 2,6-dichloro-*p*-quinonedibenzimide with hydrogen chloride contained products similar in character to those isolated in this investigation of the dipivalyl analog.

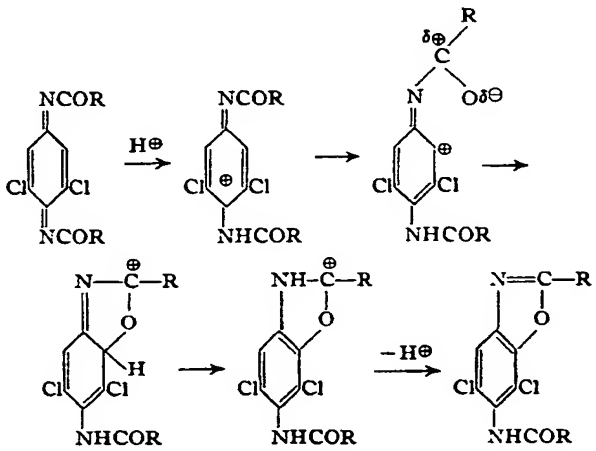
The 2,3,5-trichloro-*p*-phenylenedipivalamide was readily oxidized to the corresponding diimide which upon treatment with hydrogen chloride gave about 45% yield of the tetrachloro diamide (X). The remainder (45%) was the corresponding oxazole (XI). In the trichloro diimide a 2,6-dichloro substitution is present which appears to be the influencing factor for direct formation of an oxazole.



X XI

The benzoxazoles are probably formed by ring closure of the polarized form of the amide carbonyl. This mechanism is supported by two observations. The trichloro-*p*-phenylenedipivalamide is stable to hydrogen chloride under the conditions of the addition experiments and cannot be assumed to be an intermediate in the oxazole formation. The possibility of the participation of water is minimized by the observation that careful exclusion of water makes no significant difference in the course of the reaction. Non-formation of oxazoles from the 2,5- and 2,3-dichloro isomers with hydrogen chloride has not been explained.

In the course of this investigation, the *p*-phenylenedifluoroacetamide, *p*-phenylenedichloroacetamide and the *p*-phenylenedibenzoylacetamide were also prepared and compared qualitatively with *p*-phenylenediacetamide and *p*-phenylenedipivalamide, in respect to relative rates of oxidation by lead tetraacetate. *p*-Phenylenedifluoroacetamide was oxidized by lead tetraacetate somewhat more slowly than the acetyl or pivalyl analogs, but gave no isolable product. *p*-Phenylenedichloroacetamide was oxidized even more slowly; the quinone diimide formed was too unstable to permit purification. *p*-Phenylenedibenzoylacetamide was not oxidized at all under similar conditions.



Acknowledgment.—The authors are indebted to Miss Emily Davis, Mrs. Jean Fortney and Mrs. Katherine Pih for the microanalyses and to Miss Helen Miklas and Miss Elizabeth Petersen for the infrared spectra determinations.

Experimental

All melting points are corrected.

Pivalyl Chloride.—Pivalic acid was refluxed for one hour with excess thionyl chloride and the pivalyl chloride was purified by fractionation. The yield was nearly quantitative.

***p*-Phenylenedipivalamide.**—To a solution of 10.8 g. of *p*-phenylenediamine in 125 ml. of pyridine, 25.3 g. of pivalyl chloride was added slowly, with stirring. After standing 6 hours, the mixture was poured into excess hydrochloric acid and cracked ice. The crude product was boiled for 10 minutes with 5% hydrochloric acid, filtered, washed with water and dried. The yield of *p*-phenylenedipivalamide was 25.5 g. (93%). The product was purified from glacial acetic acid or dioxane, m.p. 283° (lit. m.p. 280°).[4]

***p*-Phenylenedibenzoylacetamide.**—Triphenylacetic acid was prepared by carbonation of triphenylmethylmagnesium chloride[5] and converted to the acid chloride.[6] A solution of 4.6 g. of triphenylacetyl chloride in 20 ml. of pyridine was added slowly, with stirring, to a solution of 0.81 g. of *p*-phenylenediamine in 10 ml. of pyridine. After standing a few minutes, the mixture was poured into a mixture of hydrochloric acid and cracked ice. The crude product weighed 4.5 g. (92.5%). Crystallization from dimethylformamide (Darco) gave a pure product, m.p. 324–326°.

Anal. Calcd. for $C_{48}H_{36}N_2O_2$: C, 85.16; H, 5.59; N, 4.32. Found: C, 85.00; H, 5.74; N, 4.45.

This product was not oxidized by lead tetraacetate either in cold or hot chloroform, benzene, glacial acetic acid, acetic anhydride, acetone, pyridine or dimethylformamide.

***p*-Phenylenedifluoroacetamide.**—A mixture of 5.0 g. of *p*-phenylenediamine and 20 ml. of trifluoroacetic acid was refluxed for 7 hours, and the mixture then poured into 400 ml. of dilute hydrochloric acid. The crude diamide was collected and washed with water. The yield was 5.9 g. (38%). Crystallization from glacial acetic acid or dioxane (Darco) gave a pure product, m.p. 274°.

(4) N. P. Buu-Hoi, *Bull. soc. chim. France*, [5] **12**, 587 (1945).
(5) H. Gilman and E. A. Zoellner, THIS JOURNAL, **51**, 3493 (1929).
(6) J. F. Norris and A. Cresswell, *ibid.*, **56**, 425 (1934.)

Anal. Calcd. for $C_{10}H_8F_6N_2O_2$: C, 40.01; H, 2.02; N, 9.33. Found: C, 40.00; H, 2.12; N, 9.46.

By refluxing this product with lead tetraacetate in chloroform for 3 hours, a red solution formed from which only tarry, amorphous materials were isolated.

Oxidation of *p*-Phenyleneditrichloroacetamide.—*p*-Phenyleneditrichloroacetamide[7] upon refluxing with lead tetraacetate in chloroform was oxidized slowly but only a low yield of an unstable product resulted.

***p*-Quinonedipivalimides.**—Equimolar amounts of the diamide and pure lead tetraacetate were refluxed in dry chloroform, for 2 hours (4 g. of diamide in 100 ml. of chloroform). The mixture was cooled and filtered to remove lead diacetate, and the chloroform distilled *in vacuo*. The residue was extracted with the petroleum ether to be used for recrystallization. Unchanged diamide was undissolved; it amounted usually to 5–10% of the material originally used. The *p*-quinonedipivalimides crystallize in lemon-yellow prisms and are soluble in the common organic solvents (Table I).

TABLE I

p-QUINONEDIPIVALIMIDES

p-Quinonedipivalimide	B.p. of petr. ether purification, °C.	Yield, %[a] (pure)	M.p., °C.	Analyses, % Calcd.	Found
Unsubst.	80–110	84	164.5	C, 70.05	70.09
				H, 8.09	8.21
				N, 10.21	10.04
2-Chloro	37–38[b]	65	81–83.5	C, 62.23	62.21
				H, 6.86	7.01
2,6-Dichloro	40–60	85	104.5–106.5	C, 55.98	55.66
				H, 5.87	5.74
2,5-Dichloro	40–60	80	159.5–160.5	C, 55.98	55.98
				H, 5.87	6.13
2,3-Dichloro	40–60	75	138.5–139.5	C, 55.98	56.08
				H, 5.87	5.86
2,3,5-Trichloro	40–60	78	115.5	C, 50.87	50.88
				H, 5.07	5.22
2,3,5,6-Tetrachloro	80–110	31	200.5–201	C, 46.62	46.54
				H, 4.40	4.62

[a] Based on unrecovered diamide. The recovered diamide was usually 5 to 10% of that used in the reaction. [b] Very soluble. Chilled in acetone–Dry Ice.

2,3,5,6-Tetrachloro-*p*-quinonedipivalimide.—The tetrachlorodiamide was not appreciably oxidized under the conditions used for the other members of this series. A mixture of 0.83 g. of tetrachloro-*p*-phenylenedipivalamide and an equimolar amount of lead tetraacetate in acetic anhydride was permitted to react with stirring at 70° for 24 hours. Upon decomposition with 500 ml. of water, a precipitate was formed. This was filtered and both precipitate and filtrate were extracted with ether. About 0.5 g. of diamide was undissolved. Upon concentration and cooling, the product separated (Table I).

Addition of Hydrogen Chloride to *p*-Quinonedipivalimides.—Hydrogen chloride was passed into a petroleum ether solution of the diimide for 10 minutes. The precipitated diamide was collected by filtration and washed with petroleum ether. The products were all obtained as colorless needles (Table II).

The hydrogen chloride addition products can be obtained without isolation of the diimides merely by passing hydrogen chloride into the petroleum ether extract of the diimide from the oxidation mixture. In this way, 2-chloro-*p*-phenylenedipivalamide was prepared in 93% yield and 2,6-dichloro-*p*-phenylenedipivalamide in 98% yield.

Stability of 2,3,5-Trichloro-*p*-phenylenedipivalamide.—In an attempt to determine whether the 2,3,5-trichloro diamide was an intermediate in the formation of the oxazole isolated when hydrogen chloride was passed into a chloroform solution of the 2,6-dichloro diamide, hydrogen chloride was passed into the trichloro diamide in chloroform for one hour. No change occurred.

2-Acetoxy-*p*-phenylenedipivalamide.—A solution of 0.69 g. of *p*-quinonedipivalimide in 10 ml. of glacial acetic acid was permitted to stand at room temperature for one day and then poured into 50 ml. of cold water. A small amount of red tar which precipitated was filtered off and discarded. Concentration of the filtrate *in vacuo* followed by chilling resulted in precipitation of 0.3 g. (36%) of 2-acetoxy-*p*-phenylenedipivalamide. Crystallization by solution in hot chloroform (Darco) and addition of hot petroleum ether (b.p. 80–110°), until the solution was just under the saturation point of the solid, gave needles, m.p. 156.5–157°.

Anal. Calcd. for $C_{18}H_{26}N_2O_4$: C, 64.65; H, 7.84; N, 8.38. Found: C, 64.91; H, 7.65; N, 8.63.

2-Formoxy-*p*-phenylenedipivalamide.—To 9 ml. of 98% formic acid, cooled in an ice-bath, 9.0 g. of *p*-quinonedipivalimide was added slowly, with stirring. The resulting red slurry was diluted to 150 ml. with cold ether, and the precipitated adduct collected. A slight additional amount of product was obtained by diluting the filtrate with an equal volume of petroleum ether (b.p. 30–60°) and chilling in acetone–Dry Ice. The total yield was 8.5 g. (81%). Purification from chloroform with addition of petroleum ether (b.p. 30–60°) gave platelets, m.p. 200–201°.

Anal. Calcd. for $C_{17}H_{24}N_2O_4$: C, 63.72; H, 7.55. Found: C, 63.99; H, 7.41.

2,5-Dipivalamidophenol. (A).—2-Acetoxy-*p*-phenylenedipivalamide was refluxed for 30 minutes with 10% aqueous sodium hydroxide, cooled, and filtered. The phenol was precipitated from the filtrate by acidification with hydrochloric acid.

The product was purified by crystallization from ether with addition of petroleum ether (b.p. 30–60°); needles, m.p. 248°. This substance gave a strong phenol test with phosphomolybdic acid and ammonia.[8]

(B).—A solution of 4.0 g. of 2-formoxy-*p*-phenylenedipivalamide in 100 ml. of ethylene glycol was boiled for 5 minutes, cooled, and diluted with an equal volume of water. The precipitated phenol weighed 3.3 g. (90%).

(C).—2-Formoxy-*p*-phenylenedipivalamide was refluxed for 15 minutes with 10% aqueous sodium hydroxide. A 77% yield of phenol resulted.

Anal. Calcd. for $C_{16}H_{24}N_2O_3$: C, 65.74; H, 8.27. Found: C, 65.80; H, 8.41.

2-*t*-Butyl-6-pivalamidobenzoxazole.—2,5-Dipivalamidophenol was dehydrated by heating the melted substance at 250° for 15 minutes in an evacuated tube (100 mm.). The cooled melt from 0.30 g. of the phenol was pulverized and triturated with 15 ml. of ether. The undissolved, undehydrated phenol weighed 0.07 g. Evaporation of the solution gave 0.18 g. (84%) of the desired benzoxazole. Recrystallization from ether–petroleum ether (b.p. 30–60°) gave platelets or needles, m.p. 164–165°.

TABLE II

p-PHENYLENEDIPIVALAMIDES PREPARED BY ADDITION OF HYDROGEN CHLORIDE TO *p*-QUINONEDIPIVALIMIDES

p-Phenylenedipivalamide	Solvent for crystn.[a]	M.p., °C.	Yield, % (pure)	Analyses, % Calcd.	Found
2-Chloro	$CHCl_3$	215	90	C, 61.83	61.86
	pet. ether (b.p. 80–110°)			H, 7.46	7.61
				N, 9.02	9.17
2,6-Dichloro[b]	$CHCl_3$	257	85	C, 55.65	55.70
	pet. ether (b.p. 80–110°)			H, 6.42	6.47
2,3,5-Trichloro	$CHCl_3$	205–206[c]	96[d]	C, 50.72	50.86
	pet. ether (b.p. 80–110°)			H, 5.58	5.65
2,3,5,6-Tetrachloro	$CHCl_3$	335–335.5	44[e]	C, 46.40	46.24
				H, 4.14	4.44

[a] Methanol was also a satisfactory solvent. The common procedure for crystallization was to dissolve in hot chloroform (Darco) and then add hot petroleum ether (b.p. 80–110°) until the mixture formed essentially a saturated solution of the solute. [b] The only isomer formed by addition of hydrogen chloride to 2-chloro-*p*-quinonedipivalimide. [c] Shrinks rapidly at 196°. [d] From 2,5-dichloro diimide, 96%; from 2,3-dichloro diimide, 97%; from 2,6-dichloro diimide, 24%. [e] About 45% of the product was the corresponding benzoxazole.

(7) L. Spirgel and P. Spiegel, *Ber.*, **40**, 1736 (1907).

(8) K. Brauer, *Chem. Ztg.*, **50**, 553 (1926).

Anal. Calcd. for $C_{16}H_{22}N_2O_2$: C, 70.05; H, 8.09; N, 10.21. Found: C, 69.96; H, 8.10; N, 10.24.

2-*t*-Butyl-6-pivalamidobenzoxazole was hydrolyzed to the phenol by refluxing for three hours with 10% aqueous sodium hydroxide.

2,5-Dichloro-*p*-phenylenedipivalamide.—This product was prepared from 2,5-dichloro-*p*-phenylenediamine dihydrochloride[9] in a manner analogous to that described for *p*-phenylenedipivalamide. The diamide was purified from chloroform and petroleum ether (b.p. 80–110°) by the procedure previously used; needles, m.p. 239–240°.

Anal. Calcd. for $C_{16}H_{22}Cl_2N_2O_2$: C, 55.65; H, 6.42. Found: C, 55.52; H, 6.34.

2,3-Dichloro-*p*-phenylenediamine.—An aqueous solution of 2,3-dichloro-*p*-phenylenediamine dihydrochloride[9] was made alkaline with sodium hydroxide solution and chilled. The precipitated diamine was purified from water to give needles, m.p. 120.5–121°.

Anal. Calcd. for $C_6H_6Cl_2N_2$: C, 40.70; H, 3.42. Found: C, 40.99; H, 3.56.

2,3-Dichloro-*p*-phenylenedipivalamide.—In a manner analogous to that described for *p*-phenylenedipivalamide, 5.0 g. of 2,3-dichloro-*p*-phenylenediamine dihydrochloride gave 4.2 g. (61%) of the diamide. It was purified from chloroform with addition of petroleum ether (b.p. 80–110°) or from methanol; needles, m.p. 200–201°.

Anal. Calcd. for $C_{16}H_{22}Cl_2N_2O_2$: C, 55.65; H, 6.42. Found: C, 55.61; H, 6.33.

2,6-Dichloro-*p*-phenylenedipivalamide.—2,6-Dichloro-*p*-phenylenediamine[2b] (m.p. 120–125°) was refluxed in pyridine for 2 hours with excess pivalyl chloride, and the mixture decomposed with ice and hydrochloric acid. The crude product was dissolved in boiling 50% acetic acid (Darco), and allowed to cool to room temperature. The crystallized material was further purified by crystallization from chloroform with addition of petroleum ether (b.p. 80–110°). The yield of pure 2,6-dichloro-*p*-phenylenedipivalamide, m.p. 256–257°, was poor. It was identical with the dichloro diamide obtained from addition of hydrogen chloride to 2-chloro-*p*-quinonedipivalimide. The infrared spectra of the two samples were identical.

Reaction of Hydrogen Chloride with 2,6-Dichloro-*p*-quinonedipivalimide.—When hydrogen chloride was passed through a solution of 2,6-dichloro-*p*-quinonedipivalimide in a minimum amount of petroleum ether (b.p. 80–110°) for about 10 minutes the solution was decolorized. A small amount of precipitate that separated was filtered. Repeated recrystallization of this precipitate from aqueous ethanol and finally from chloroform with addition of petroleum ether (b.p. 80–110°) yielded a small amount of 2,6-dichloro diamide. Analysis of the more soluble material indicated it was impure 2,3,5-trichloro-*p*-phenylenedipivalamide.

Concentration of the original mother liquor gave another white precipitate which was fractionated from 50% ethanol into a (1) more soluble, lower-melting neutral substance later identified as an oxazole and (2) a less soluble, higher-melting acidic substance which proved to be the phenol corresponding to the oxazole.

Since the crystallization procedure proved to be tedious and unsatisfactory, a chromatographic method was used.

Hydrogen chloride was passed into a solution of 7.0 g. of 2,6-dichloro-*p*-quinonedipivalimide in 250 ml. of petroleum ether (b.p. 80–110°) for 10 minutes. The solution was decolorized and a precipitate formed. This mixture was boiled to remove excess hydrogen chloride, and was brought into complete solution at room temperature by adding a minimum amount (about 8 l.) of a solvent mixture consisting of 75% petroleum ether (b.p. 80–110°) and 25% dry ethyl ether. The solution was passed (5 ml. per minute) through a 3.5 × 100 cm. column of activated alumina (80–200 mesh) and the solute was adsorbed. The column was developed with 10 l. of the same solvent mixture. Continued use of this solvent, taking 100-ml. cuts and evaporating to dryness, eluted first 2.3 g. (33%) of 2-*t*-butyl-5,7-dichloro-6-pivalamidobenzoxazole (8 l. of solvent used), then 1.6 g. (24%) of 2,3,5-trichloro-*p*-phenylenedipivalamide (15 l. solvent). The solvent was changed to dry ethyl ether, and 1.0 g. (15%) of 2,6-dichloro-*p*-phenylenedipivalamide was finally eluted. This procedure gave a clean separation of the products.

Since the reaction flask had been open to the atmosphere in the experiment just described, a second experiment was performed with special precautions against the presence of moisture. The diimide was dried in a desiccator over phosphorus pentoxide. The petroleum ether and the hydrogen chloride were also carefully dried and the reaction flask protected from the atmospheric moisture. After removing excess of hydrogen chloride with dry air, the product was worked up as before. It did not differ essentially from that obtained in the first experiment.

2-*t*-Butyl-5,7-dichloro-6-pivalamidobenzoxazole.—The first product from the column formed colorless needles, m.p. 164.5–165.5°. For analysis, the sample was adsorbed on alumina from petroleum ether, eluted with ethyl ether and recrystallized once from petroleum ether, m.p. 165.5–167.5°. Attempts to crystallize from methanol resulted in partial hydrolysis with a spreading of the melting point.

Anal. Calcd. for $C_{16}H_{20}Cl_2N_2O_2$: C, 55.99; H, 5.87; N, 8.16; Cl, 20.66. Found: C, 55.51, 55.56; H, 5.91, 5.71; N, 7.58; Cl, 21.09.

3,6-Dipivalamido-2,4-dichlorophenol. (A).—A suspension of 0.4 g. of 2-*t*-butyl-5,7-dichloro-6-pivalamidobenzoxazole in 25 ml. of 10% aqueous sodium hydroxide and 5 ml. of ethanol was refluxed for 4 hours. The solution was cooled and filtered and the filtrate acidified with hydrochloric acid. The precipitated phenol was collected by filtration. The yield was 0.37 g. (88%). After purification from ether with addition of petroleum ether (b.p. 30–60°) it formed needles, m.p. 226° (with loss of water). The product dissolves slowly in 5% aqueous sodium bicarbonate.

Anal. Calcd. for $C_{16}H_{22}Cl_2N_2O_3$: C, 53.20; H, 6.14; N, 7.76; Cl, 19.63. Found: C, 53.04; H, 6.09; N, 8.01; Cl, 19.59.

This compound is identical with the phenol first isolated by crystallization, as shown by the melting points of mixtures and infrared spectra.

A solution of 3,6-dipivalamido-2,4-dichlorophenol in ethylene glycol was boiled for 10 minutes, cooled and extracted with ether. Evaporation of the ether gave a nearly quantitative yield of 2-*t*-butyl-5,7-dichloro-6-pivalamidobenzoxazole. After one recrystallization, it melted at 164–166° and did not depress the melting point of an authentic sample.

(B).—Chlorine was passed into a solution of 2.0 g. of 2,5-dipivalamidophenol in 100 ml. of glacial acetic acid at 20°, until the weight had increased by 0.95 g. (for 2 moles of chlorine, 0.98 g.). The resulting solution was poured into 600 ml. of cold water, and the precipitate filtered.

The less acidic components of the chlorination mixture were precipitated by passing carbon dioxide for 2 hours through a solution of the crude product in 75 ml. of 5% aqueous sodium hydroxide, and then removed by filtration. Acidification of the filtrate with hydrochloric acid gave 3,6-dipivalamido-2,4-dichlorophenol, which was further purified by recrystallization from chloroform with addition of petroleum ether (b.p. 30–60°). The yield was 0.3 g. (12%). This substance did not depress the melting point of the phenol obtained from the addition of hydrogen chloride to 2,6-dichloro-*p*-quinonedipivalimide, and the infrared spectra of the two were identical.

3,6-Dipivalamido-2,4-dichlorophenyl Acetate.—To a solution of 0.12 g. of 3,6-dipivalamido-2,4-dichlorophenol in 20 ml. of water and 0.5 ml. of 5% aqueous sodium hydroxide, 0.04 ml. of acetic anhydride was added with rapid stirring at ice-bath temperature. The precipitated acetate weighed 0.10 g. (83%) and was purified from chloroform with addition of petroleum ether (b.p. 80–110°), m.p. 267–268°.

Anal. Calcd. for $C_{18}H_{24}Cl_2N_2O_4$: C, 53.60; H, 6.00. Found: C, 53.79; H, 5.99.

2,5-Dipivalamido-3,4-dichlorophenol.—A solution of 0.3 g. of 2,3-dichloro-*p*-quinonedipivalimide in 5 ml. of 98% formic acid was allowed to stand at room temperature for 30 minutes. The resulting red solution was diluted with 75 ml. of ether and extracted with 100 ml. of 5% aqueous sodium hydroxide. Upon acidification with hydrochloric acid, 0.2 g. (63%) of the phenol was precipitated. The product was purified from chloroform with addition of pe-

(9) R. Adams, E. F. Elslager and K. F. Heumann, THIS JOURNAL, 74, 2608 (1952).

troleum ether (b.p. 30–60°), m.p. 190.5–191°. This product is not appreciably soluble in 5% aqueous sodium bicarbonate.

Anal. Calcd. for $C_{16}H_{22}Cl_2N_2O_2$: C, 53.20; H, 6.14. Found: C, 53.46; H, 6.27.

2,5-Dipivalamido-3,6-dichlorophenol.—In a manner similar to that used for the 2,5-dipivalamido-3,4-dichlorophenol, formic acid was added to 0.5 g. of 2,5-dichloro-*p*-quinonedipivalimide to give an adduct which upon hydrolysis yielded 0.23 g. (44%) of 2,5-dipivalamido-3,6-dichlorophenol. The product was purified from chloroform with addition of petroleum ether (b.p. 30–60°), m.p. 199.5–200.5°. This product is not appreciably soluble in 5% aqueous sodium bicarbonate.

Anal. Calcd. for $C_{16}H_{22}Cl_2N_2O_3$: C, 53.20; H, 6.14. Found: C, 53.39; H, 5.98.

2,3,5,6-Tetrachloro-*p*-phenylenedipivalamide.—A solution of 2.5 g. of tetrachloro-*p*-phenylenediamine,[2b] and 2.5 g. of pivalyl chloride in 25 ml. of pyridine was refluxed for 4.5 hours, then cooled and poured into ice and hydrochloric acid. The crude diamide weighed 4.0 g. (95%). It was recrystallized from 95% ethanol and finally from chloroform; platelets, m.p. 335–335.5°. This product proved to be identical to that formed by addition of hydrogen chloride to the 2,3,5-trichloro diimide.

Addition of Hydrogen Chloride to 2,3,5-Trichloro-*p*-quinonedipivalimide.—Hydrogen chloride was passed into a solution of 0.25 g. of 2,3,5-trichloro-*p*-quinonedipivalimide in petroleum ether (b.p. 80–110°). The precipitate that formed was removed by filtration, and identified as tetrachloro-*p*-phenylenedipivalamide, 0.12 g. (44%). Concentration of the filtrate gave 0.11 g. (45%) of colorless needles which were crystallized from petroleum ether (b.p. 80–110°) and aqueous ethanol; m.p. 225°. The product analyzed for the corresponding oxazole, 2-*t*-butyl-4,5,7-trichloro-6-pivalamidobenzoxazole.

Anal. Calcd. for $C_{16}H_{19}Cl_3N_2O_2$: C, 50.87; H, 5.07; N, 7.42. Found: C, 50.58; H, 4.96; N, 7.84.

Upon refluxing this product for 4 hours with 10% aqueous sodium hydroxide and acidifying, a low yield of a phenol resulted.

URBANA, ILLINOIS

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE OHIO STATE UNIVERSITY]

Addition Reactions of Nitroalkanes with Acrolein and Methyl Vinyl Ketone. Selective Reduction of Nitrocarbonyl Compounds to Nitrocarbinols

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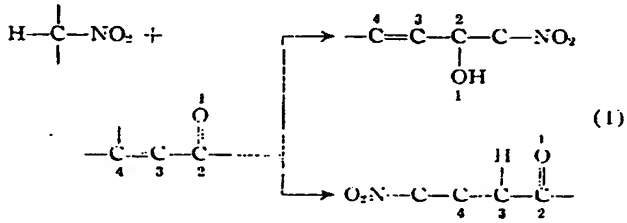
Reactions of nitromethane, nitroethane and 2-nitropropane with methyl vinyl ketone and acrolein in the presence of benzyltrimethylammonium hydroxide or sodium methoxide result principally in 1,4-addition to give the corresponding nitrocarbonyl compounds. General techniques have been developed for the selective reduction of aliphatic primary, secondary and tertiary mononitro and primary and secondary *gem*-dinitro aldehydes and ketones to their corresponding mononitro and dinitrocarbinols by reaction with (1) aluminum isopropoxide in 2-propanol or toluene or (2) sodium borohydride in water–methanol.

Discussion

The present investigation consists of (1) a continuation of a study of addition reactions of acidic nitroalkanes with acrolein and methyl vinyl ketone[3] and (2) the development of general methods for the selective reduction of the nitrocarbonyl compounds produced therefrom into the corresponding nitrocarbinols.

Nitrocarbonyl Compounds.—Reaction of a nitroalkane with an α,β-unsaturated carbonyl compound (Equation 1) may occur with (1) the carbonyl



(1)

group to yield the unsaturated nitrocarbinol and (2) the carbon–carbon double bond to give the corresponding saturated nitrocarbonyl derivative. In the base-catalyzed condensation of nitroparaffins with conjugated unsaturated ketones, it has been demonstrated that the principal reaction is addition of the nitro compound to the olefinic linkage.[3,4] The reaction of nitroalkanes with certain substituted α,β-unsaturated aldehydes is reported to involve either or both 1,2- and 1,4-addition[5]; this system, however, has not been extensively studied.

In the present study it has been found that reactions of 2-nitropropane, nitroethane and nitromethane with acrolein and methyl vinyl ketone, catalyzed by benzyltrimethylammonium hydroxide or sodium methoxide, result principally in addition to the olefinic groups of the conjugated carbonyl compounds (Table I). The yields of 1:1 addition products obtained from the nitroalkanes decrease in the order: 2-nitropropane > nitroethane > nitromethane, and are much greater with methyl vinyl ketone than with acrolein. The variation in yields obtained with the nitroalkanes is attributed to the difference in the number of replaceable hydrogens of the acidic nitro compounds. Thus, 2-nitropropane gives rise to only 1:1 addition products, whereas nitroethane and nitromethane also yield 1:2, and 1:2 and 1:3 adducts, respectively. Maximum yields of the 1:1 adducts were realized when higher

(1) Taken in part from the (a) M.S. thesis of D. E. Ley, August, 1951, and (b) Ph.D. Dissertation of L. Zeldin, June, 1951.

(2) Financial support of the research of L. Zeldin was supplied by the Office of Naval Research.

(3) H. Shechter and L. Zeldin, THIS JOURNAL, 73, 1276 (1951).

(4) E. P. Kohler, *ibid.*, 38, 889 (1916); 46, 503 (1924); E. P. Kohler and H. F. Engelbrecht, *ibid.*, 41, 1379 (1919); E. P. Kohler and H. E. Williams, *ibid.*, 41, 1644 (1919); E. P. Kohler and M. S. Rao, *ibid.*, 41, 1697 (1919); E. P. Kohler and L. I. Smith, *ibid.*, 44, 624 (1922); M. C. Kloetzel, *ibid.*, 69, 2271 (1947).

(5) E. F. Degering and A. Sprang, U. S. Patent 2,332,482 (October 19, 1943); G. Fort and A. McLean, *J. Chem. Soc.*, 1907 (1948); P. J. Villani and F. F. Nord, THIS JOURNAL, 69, 2608 (1947); D. T. Warner and O. A. Moe, *ibid.*, 74, 1064 (1952).